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## PATTERNED CERAMIC FILMS AND METHOD FOR PRODUCING THE SAME

### BACKGROUND

Fuel cells use an electrochemical energy conversion of fuel (including but  
10 not limited to hydrogen, propane, methane, carbon monoxide, and the like) and  
oxidant(s) into electricity and heat. It is anticipated that fuel cells may be able to  
replace primary and secondary batteries as a portable power supply. In fuel cells,  
the fuel (usually containing a source of hydrogen) is oxidized typically with a source  
of oxygen to produce (primarily) water and carbon dioxide. The oxidation reaction  
15 at the anode, which liberates electrons, in combination with the reduction reaction  
at the cathode, which consumes electrons, results in a useful electrical voltage and  
current through the load.

As such, fuel cells provide a direct current (DC) voltage that may be used to  
power motors, lights, electrical appliances, etc. A solid oxide fuel cell (SOFC) is  
20 one type of fuel cell that may be useful in portable applications. The material  
properties, which are generally desirable for obtaining high performing fuel cell  
devices, also make fabrication of those fuel cell devices a significant challenge.

### BRIEF DESCRIPTION OF THE DRAWINGS

25 In the drawings, like reference numerals correspond to similar, though not  
necessarily identical components. For the sake of brevity, reference numerals  
having a previously described function may not necessarily be described in  
connection with subsequent drawings in which they appear.

Fig. 1A is a perspective front view of an embodiment of the present invention, showing an embodiment of a liquid film deposited on an embodiment of a substrate;

Fig. 1B is a view similar to Fig. 1A, showing an embodiment of a mask on a predetermined portion of an embodiment of the liquid film;

Fig. 1C is a view similar to Fig. 1A, showing an embodiment of a patterned liquid film;

Fig. 2A is a perspective front view of an alternate embodiment of the present invention, showing an embodiment of a liquid film deposited on an embodiment of a substrate;

Fig. 2B is a view similar to Fig. 2A, showing an embodiment of a mask on a predetermined portion of an embodiment of the liquid film;

Fig. 2C is a view similar to Fig. 2A, showing an embodiment of the patterned liquid film;

Fig. 3 is a scanning electron micrograph (SEM) at 35X magnification showing a top view of an embodiment of a patterned ceramic film according to an embodiment of the present invention; and

Fig. 4 is a schematic view of an embodiment of the fuel cell according to an embodiment of the present invention.

## DETAILED DESCRIPTION OF THE EMBODIMENTS

It was discovered that novel patterned ceramic films may be made relatively simply, quickly, and efficiently through use of a liquid precursor solution in conjunction with patterning and heating techniques. These patterned ceramic films may be used in various applications, including ion-conducting ceramics, patterned electrodes in fuel cells, hard ceramic coatings, transparent conducting oxides, and transparent semiconducting oxides.

Referring now to Fig. 1A, an embodiment for making a patterned ceramic film includes the step of depositing a liquid precursor solution onto a substrate 14 to form a liquid film 12.

It is to be understood that any suitable material may be chosen for the substrate 14. In an embodiment, the substrate 14 is single crystal silicon, polycrystalline silicon, silicon oxide containing dielectric substrates, alumina, sapphire, ceramic, and/or mixtures thereof. In an alternate embodiment of the present invention, a silicon wafer is the substrate 14 of choice.

In an embodiment, the liquid precursor solution is made by dissolving one or more metal salts in a photoresist. It is to be understood that any suitable metal salt(s) (non-limitative examples of the salt component of the metal salt(s) include nitrates, sulfates, and/or chlorides) may be chosen that do not overly contaminate the patterned ceramic film as observed by desired electrical, chemical, and/or mechanical performance, and/or reliability. In an embodiment, the metal salts are cerium nitrate and/or samarium nitrate.

Many metal salts are soluble in water. Therefore, dissolution of the metal salts would be easily achieved if a water-soluble photoresist were used. However, most photoresists are not water-soluble. It is to be understood that the photoresist may act as a carrier for the metal salt(s).

It is to be understood that some standard photoresists used in photolithography may, in some instances, not be suitable in embodiment(s) of the method. It is to be understood that replacing the photoresists useful for embodiments of the present invention with conventional photoresists may, in some instances, not result in a suitable ceramic film after heating. Without being bound to any theory, it is believed that a desirable photoresist will possess functional groups capable of stabilizing the metal cation to promote a substantially homogeneous liquid precursor solution. One non-limitative example of a suitable photoresist is one which has ketone groups on the ends of the repeat unit which may act to coordinate the metal cation. A non-limitative example of photoresists suitable for embodiments of the present invention include diacrylates. In an embodiment, the photoresist is tetra-ethylene glycol diacrylate, polyvinylphenol (PVP), poly(4-vinylphenol), poly(4-hydroxystyrene), and/or any DNQ (diazonaphthoquinone)-Novolak based resist.

It is to be understood that the amount of metal salt(s) used depends upon the chosen metal salt and its solubility. In an embodiment, the concentration of metal salt to photoresist may be up to about 5 moles of metal per liter of photoresist.

5           It is to be understood that the liquid precursor solution is a true solution of the metal salts substantially fully dissolved in the photoresist. In order to obtain a fully miscible liquid precursor solution, the solution may be mixed until substantially all of the solids are dissolved into the photoresist. A fully miscible solution generally has no powder particles therein. Such a fully miscible solution may be  
10   advantageous for many reasons, for example, when the line-widths to be patterned are equal to or smaller than the size of the powder particles.

          Generally, the time it takes to substantially fully dissolve the metal salts into the photoresist depends on the materials used. In an embodiment of the present invention, the total dissolution time is about two hours. If the metal salts are not  
15   substantially completely dissolved, the resulting liquid film 12 may possess undesirable heterogeneous properties.

          In an embodiment of the present invention, one or more additives may optionally be mixed into the liquid precursor solution before it is deposited on the substrate 14. The addition of additives may assist in the thermal and ultraviolet  
20   curing of the liquid precursor solution after it is applied to the substrate 14. It is to be understood that any suitable additives may be chosen. In an embodiment, suitable photoinitiator additives include, but are not limited to 2,5 dimethyl 2,5-di-*t*-butylperoxy hexane (commercially available under the tradename LUPEROX 101 from ATOFINA Chemicals Inc. in Philadelphia, Pennsylvania), alpha, alpha-  
25   dimethoxy-alpha-phenylacetophenone (commercially available under the tradename IRGACURE 651 from Ciba Specialty Chemicals in Terrytown, New York), and/or mixtures thereof.

          In an embodiment of the present invention, the liquid precursor solution is deposited onto the substrate 14 using deposition techniques including, but not  
30   limited to, spin coating, screen printing, dip coating, meniscus coating, and spray

coating. Spin coating generally forms very thin film thicknesses and small, intricate geometries. In an embodiment, the thin film thicknesses are less than or equal to about 1  $\mu\text{m}$ . Screen printing generally forms thicker film thicknesses and larger geometries. In an alternate embodiment, the thicker film thicknesses are greater than or equal to about 10  $\mu\text{m}$ .

In an embodiment, the liquid film 12 ranges in thickness from about 0.05  $\mu\text{m}$  to about 0.5  $\mu\text{m}$ . In an alternate embodiment, the liquid film 12 has a thickness of about 0.25  $\mu\text{m}$ .

It is to be understood that a thicker liquid film 12 according to an embodiment of the present invention may be formed by depositing multiple layers 12 of the liquid precursor solution onto the substrate 14.

Now referring to Fig. 1B, the method of the embodiment of the present invention further includes the step of patterning the liquid film 12. It is to be understood that liquid film 12 may be patterned into any suitable shape, size and/or configuration.

Any applicable negative or positive photolithography technique may be selected to pattern the liquid film 12.

In an embodiment, patterning includes the step of masking a portion of the liquid film 12. A mask 16 is placed over the liquid film 12 such that one portion 22 of the liquid film 12 is masked and another portion 24 of the liquid film 12 is unmasked.

The patterning step further includes the step of exposing the liquid film 12, with the mask 16 thereon, to a light source 18. It is to be understood that any suitable light source 18 may be used. In an embodiment of the present invention, a UV lamp (365 nm 200 W/lin. in) is exposed to the liquid film 12. The light source 18 cures either the masked 22 or the unmasked 24 portion of the liquid film 12 (depending upon whether positive or negative photolithography is used).

Fig. 1B shows a non-limitative example of an embodiment of the present invention whereby a positive photolithography technique is used. With this

technique, the masked portion 22 of the liquid film 12 is cured, and the unmasked portion 24 of the liquid film 12 is uncured.

5 In an embodiment of the present invention, after the liquid film 12 is exposed to the light source 18, the method may further optionally include the step of baking the liquid film 12. It is to be understood that this post-exposure bake may be a low temperature bake. In an embodiment, the bake temperature ranges between about 50°C and about 250°C. In an alternate embodiment, the bake temperature is about 100°C.

10 Referring now to Fig. 1C, in an embodiment of the method of the present invention, the patterning step further includes the step of removing the uncured portion of the liquid film 12, leaving the patterned liquid film 20. It is to be understood that removal of the uncured portion of the liquid film 12 may be accomplished by any suitable means, including but not limited to solvent stripping. In an embodiment, removal occurs by dissolving the uncured portion of the liquid  
15 film 12 in isopropyl alcohol.

In an embodiment, the method includes the step of heating the patterned liquid film 20 to drive off the organics that remain from the liquid precursor solution. It is to be understood that any suitable heat treatment may be chosen. In an embodiment, the patterned liquid film 20 is fired at temperatures ranging between  
20 about 550°C and about 600°C. In a further embodiment, the firing temperature ranges between about 540°C and about 1050°C. It is to be understood that, in some instances, higher temperatures may aid in removing contamination, and/or achieving the desired morphology or phase of the patterned ceramic film 10.

25 It is to be understood that the line width W of the patterned liquid film 20 may be any suitable width; however in an embodiment, the width ranges between about 0.5  $\mu\text{m}$  to about 2 mm.

Embodiment(s) of the patterned ceramic film 10 may have thicknesses ranging between about 0.2  $\mu\text{m}$  and about 0.3  $\mu\text{m}$ . It is to be understood that

patterned ceramic films 10 having thicknesses in this range are substantially crack free.

Referring now to Figs. 2A through 2C, an embodiment for making a patterned ceramic film 10 includes the steps as described hereinabove in relation to Figs. 1A through 1C. In contrast, however, referring particularly to Fig. 2B, the patterning step uses a negative photolithography technique. A mask 16 is placed over a portion of the liquid film 12 such that a portion 22 of the liquid film 12 is masked and a portion 24 of the liquid film 12 is unmasked.

In this embodiment using negative photolithography, the masked portion 22 is uncured, and the unmasked portion 24 of the liquid film 12 is cured.

Referring now to Fig. 2C, the method of the embodiment of the present invention further includes the step of removing the uncured portion 24 of the liquid film 12. Fig. 2C shows an alternate embodiment of the present invention wherein the patterned liquid film 20' is a reverse configuration of the mask 16 used (shown in Fig. 2B).

To further illustrate, the following example is given. It is to be understood that this example is provided for illustrative purposes and is not to be construed as limiting the scope of the claimed subject matter.

## EXAMPLE

6.94 g of cerium nitrate and 1.78 g of samarium nitrate were added to 40 cc of tetra-ethylene glycol diacrylate to form the liquid precursor solution. 5 cc of LUPEROX™ photoinitiator and 5% by weight of IRGACURE 651 were added to the liquid precursor solution to assist in thermal and ultraviolet curing. The solution was mixed for about 2 hours so that the mixture was completely dissolved and a clear solution was obtained.

The liquid precursor solution was then spin coated onto a silicon wafer. Shadow masking and ultraviolet exposure were used to pattern the liquid film. After exposure, the uncured portion of the patterned liquid film was removed with isopropyl alcohol. The patterned liquid film was then fired at about 540°C to

remove the organic portion of the liquid precursor solution and to leave the desired samarium doped ceria (SDC) patterned ceramic film. This SDC patterned film may be suitable for use as an anode in a fuel cell (for example, in a solid oxide fuel cell (SOFC)).

5 Referring now to Fig. 3, a SEM at 35X magnification of a top view of the resultant SDC patterned ceramic film is shown.

It is to be understood that the embodiments of the patterned ceramic films may be used in a variety of applications, including, but not limited to, ion-conducting ceramics (for example, electrolytes), hard ceramic coatings, transparent  
10 conducting oxides (a non-limitative embodiment of which is indium tin oxide) and transparent semiconducting oxides (a non-limitative example of which is zinc oxide), ferroelectric oxides (a non-limitative example of which is lead zirconate titanate), dielectric oxides (non-limitative examples of which include aluminum oxides and zirconium oxides), and as anodes and cathodes. The electrolytes,  
15 anodes and cathodes may be suitable for use in fuel cells.

Referring now to Fig. 4, in an embodiment of the present invention, a fuel cell 100 includes at least one electrode 26, 30 in electrochemical contact with an electrolyte 28. It is to be understood that the electrode 26, 30 may be an anode 26 or a cathode 30. It is to be further understood that the electrolyte 28, the anode 26,  
20 and/or the cathode 30 may be a patterned ceramic film 10 according to embodiment(s) of the present invention.

Fig. 4 is a simplified schematic diagram of a dual chamber fuel cell 100. It is to be understood that fuel cell 100 may also be a single chamber fuel cell.

Further, it is to be understood that the fuel cell 100 may be one of solid  
25 oxide fuel cells, proton conducting ceramic fuel cells, Polymer Electrolyte Membrane (PEM) fuel cells, molten carbonate fuel cells, solid acid fuel cells, and Direct Methanol PEM fuel cells.

In the fuel cell 100 embodiments of the present invention, oxidants 34 are carried to the cathode 30, and reactants 32 are carried to the anode 26. In an  
30 embodiment, the reactants 32 are fuels, and the oxidants 34 are one of oxygen, air,



and mixtures thereof. It is to be understood that any suitable fuel/reactant 32 may be used with the fuel cell 100. In an embodiment, the fuel/reactant 32 is selected from at least one of hydrogen, methane, ethane, propane, butane, pentane, methanol, ethanol, higher straight chain or mixed hydrocarbons, for example,

5 natural gas or gasoline (low sulfur hydrocarbons may be desirable, e.g. low sulfur gasoline, low sulfur kerosene, low sulfur diesel), and mixtures thereof. In an alternate embodiment, the fuel/reactant 32 is selected from the group consisting of butane, propane, methane, pentane, and mixtures thereof. Suitable fuels may be chosen for their suitability for internal direct reformation, suitable vapor pressure  
10 within the operating temperature range of interest, and like parameters.

It is to be understood that if fuel cell 100 is a single chamber fuel cell, a gaseous mixture of reactant 32 and oxidant 34 may be directed toward the anode 26 and/or the cathode 30.

An embodiment of a method of using fuel cell 100 includes the step of  
15 operatively connecting the fuel cell 100 to electrical load L and/or to electrical storage device S. The electrical load L may include many devices, including, but not limited to any or all of computers, portable electronic appliances (e.g. portable digital assistants (PDAs), portable power tools, etc.), and communication devices, portable or otherwise, both consumer and military. The electrical storage device S  
20 may include, as non-limitative examples, any or all of capacitors, batteries, and power conditioning devices. Some exemplary power conditioning devices include uninterruptible power supplies, DC/AC converters, DC voltage converters, voltage regulators, current limiters, etc.

It is also contemplated that the fuel cell 100 may, in some instances, be  
25 suitable for use in the transportation industry, e.g. to power automobiles, and in the utilities industry, e.g. within power plants.

An embodiment of a method of using a patterned ceramic film 10 includes the step of operatively disposing the patterned ceramic film 10 in a device. It is to be understood that any suitable device may be chosen such that the patterned  
30 ceramic film 10 is adapted to be used as an ion-conducting ceramic, an electrode,

hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and/or dielectric oxides.

Embodiments of the present invention may provide many advantages, examples of which include, but are not limited to the following. Embodiments of the present invention may advantageously provide a method of making patterned ceramic films while generally avoiding having to pattern the hard and brittle ceramic film. Further, embodiments of the patterned ceramic film 10 may be advantageously used as ion-conducting ceramics, electrodes, hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and/or dielectric oxides.

While several embodiments of the present invention have been described in detail, it will be apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting, and the true scope is that defined in the following claims.